

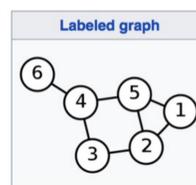
Introduction

- Spectroscopic characterization of chloride molten salts with high f-element loading is relevant to nonproliferation and online monitoring of molten salt reactors.
- Ab initio* molecular dynamic (AIMD) simulations based on density functional theory and the Born-Oppenheimer approximation have modeled UCl_3 in a LiCl-KCl eutectic over varying actinide concentration and temperature to determine changes in local environment and vibrational density of states.
- The atomistic resolution from simulation provides an opportunity to monitor changes in local coordination environment and uniquely identify their spectroscopic signatures.

Methods and analysis

- The AIMD simulations were carried out using the CP2K package using recently developed basis sets and pseudopotentials for the actinide series.¹ The simulation cells contained 3.0-100 mol % UCl_3 in a roughly 60:40 LiCl-KCl eutectic.
- Simulations were carried out in the NVT ensemble at 1150 K, higher than the melting temperature across the phase diagram, using a 0.5 fs time step for approximately 20 fs after equilibration.

- Networks of intermolecular interactions were first created, where individual ions are nodes and intermolecular interactions are edges.²
- Edge definitions utilize geometric criterion based upon the position of the radial distribution functions for relevant pairs.



Adjacency matrix
$\begin{pmatrix} 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 1 \\ 1 & 1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix}$

Eigendecomposition

$$\begin{bmatrix} a_{11} & \dots & a_{1n} \\ a_{21} & \dots & a_{2n} \\ \vdots & \ddots & \vdots \\ a_{n1} & \dots & a_{nn} \end{bmatrix} \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{bmatrix} = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}$$

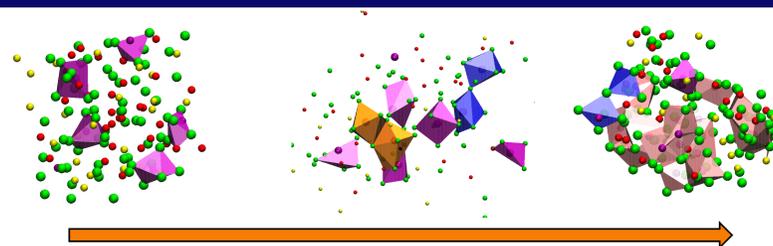
- Eigenvalue spectrum and eigenvectors reflect graph connectivity
- We use PageRank as a descriptor to identify polyhedra in concentrated electrolytes

$$PR(p_i) = \frac{1-d}{N} + d \sum_{p_j \in M(p_i)} \frac{PR(p_j)}{L(p_j)}$$

Number of vertices	Polygon name	Shape	PageRank
4	Square		0.2441558
4	Tetrahedron		0.2000000
5	Square pyramid		0.1892430

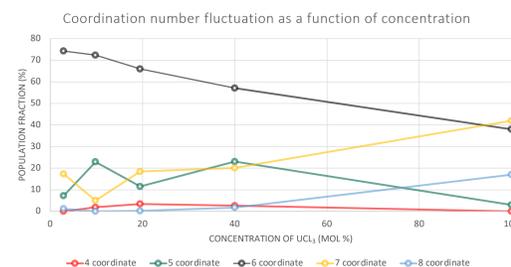
- PR values uniquely identify polyhedral coordination environments about ions
- Deformations are included in algorithm by allowing for a range of edge-widths that occur during dynamic evolution of polygons in time

Coordination Changes



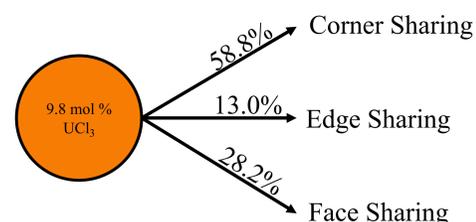
Concentration of UCl_3

- UCl_6 octahedral complexes form at 3 mol % as isolated octahedrons. At increasing $[\text{UCl}_3]$, chloride start to bridge polygon coordination environments via corner, edge, and face sharing geometries.³

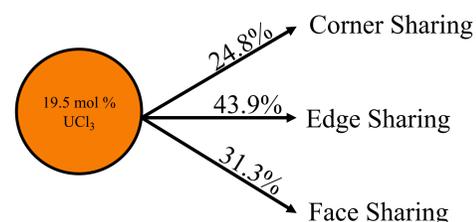


Mol % of UCl_3	Coordination Number
3.0	6.12
9.8	5.74
19.5	6.01
39.1	6.10
100	6.80

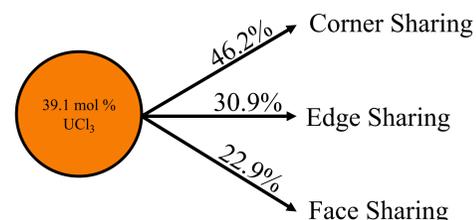
Polyhedra Networks



C.N.	Corner (%)	Edge (%)	Face (%)
4	0	0	0
5	81	24	0
6	18	76	57
7	1	0	43
8	0	0	0



C.N.	Corner (%)	Edge (%)	Face (%)
4	40	30	5.0
5	35	18	18
6	12	14	10
7	13	22	20
8	0	16	47

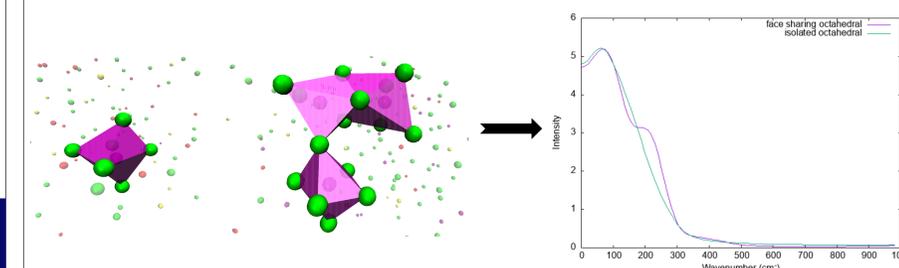


C.N.	Corner (%)	Edge (%)	Face (%)
4	12	14	5
5	16	17	9
6	15	14	17
7	22	30	31
8	35	25	38

Spectroscopic Signatures

Power Spectrum

- The vibrational density of states (VDOS) or power spectrum of the autocorrelation function was calculated for the global system and for connected polyhedral with extended lifetimes.
- The objective was to determine if the change in speciation lead to observable shifts in the vibrational spectra that could be adopted in online monitoring applications.
- Capturing an ensemble of coordination environments via AIMD simulations allows for the comparison against experimental data whilst having the advantage of identifying the contribution of different polyhedra vibrational signatures and omitting the background LiCl-KCl from the spectrum.
- The isolated UCl_6 octahedral and face sharing polyhedra had extended lifetimes sufficient for the determination of their VDOS, depicted below.



- The peak at $\sim 100 \text{ cm}^{-1}$ is indicative of the octahedral structure and the introduction of the peak at $\sim 230 \text{ cm}^{-1}$ is presumed to be from the face sharing dimer.

Future Work

RAMAN/IR Spectroscopy

- Molecular Dynamic simulations carried out for this work are being used for the determination of both the RAMAN and IR spectra using newly implemented techniques in the TRAVIS package.⁴

Experimental Collaboration

- Our collaborators at the Colorado Schools of Mines are finalizing their molten salt furnace and spectroscopy design which in turn will allow for our work to help analyze their results at the atomic level.

References

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